Economic and Environmental Impact of Traditional Rust Preventives as Compared to Novel Biobased Temporary Coatings

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Abstract: Biobased temporary rust preventatives are gaining market share due to their low cost, effectiveness and excellent environmental profile. Traditional petroleum derived rust preventatives require expensive degreasers and hazardous disposal methods, while biobased products are inherently biodegradable and in most cases do not require removal before painting or welding. Additionally, today's trends in automotive industry move towards sustainable and renewable materials which make USDA certified, biobased, temporary rust preventatives an excellent alternative for petroleum derived coatings.

This paper includes comparative experimental testing of biobased and petroleum based rust preventatives in humidity chamber according to ASTM D-1748. The corrosion protection efficiency was determined using polarisation techniques according to ASTM G5-94 on Potentiostat/Galvanostat 273A EG&E.

Keywords: rust preventatives, biobased, temporary protection, corrosion testing

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Introduction

Temporary corrosion protection of metal components and surfaces during shipment, storage, and/or in between manufacturing processes, is critical to a variety of industries worldwide. A common example of this is automotive components, which may require temporary corrosion protection for a few days, weeks, or months. Rust preventative liquids are regularly used to accomplish this task.

When choosing a temporary rust preventative product, multiple considerations must be made. In addition to effective corrosion protection, the product should provide little to no interference with the function of the metal part or surface, and should also be safe and friendly to the environment and the workers using it. Finally, ease of removal needs to be considered. Traditionally, oil- and solvent-based products have been used for the preservation of metals during shipment, storage, or between processes. While these products may offer sufficient corrosion protection, they often contain hazardous ingredients and are not readily biodegradable [2, 2]. As environmental and disposal regulations become more and more stringent, the desire for "green" corrosion inhibitors is increasing [3]. Recently, the use of bio-based products, derived from vegetable oils and their esters, has been found to offer equal or better corrosion protection properties, when compared to their petroleum derived counterparts [2].

There are three main requirements of effective temporary rust preventative. First, the substance must bind itself to the metal surface. Second, the rust preventative should provide a barrier against moisture. Finally, the rust preventative should effectively and evenly cover the metal surface. Traditional temporary rust preventatives utilise oils which contain organic compounds such as fatty acids. These compounds form a physical barrier between the metal substrate and the corrosive environment [4]. The fatty acid molecules have a long water-repelling hydrocarbon tail and a head that has a strong affinity for the metal surface [5, 6]. However, over time, moisture will diffuse through the oil layer to the metal surface. To combat this, more recent formulations of rust preventatives will form a layer and prolong the rust protection period. Rust preventatives provide corrosion protection of the metal, while the carrier ensures the efficient spread over the complete metal surface [7].

Different approaches can be used to create an environmentally friendly rust preventative system. The most common method is to replace solvent- or oil-based carriers in formulations with water-based technology. The second option is to replace petroleum-based carriers with solvents manufactured from environmentally friendly renewable resources. This has been accomplished by combining VCIs with soy-derived and canola oils, creating anticorrosion product formulations for many different applications. The last method is to utilize biodegradable VCI chemistry building blocks in conventional solvent carriers [2].

This paper will be focused on the first approach. Laboratory test results, as well as economic and environmental impact of traditional rust preventatives will be compared to a novel water/bio-based product. The goal of this research is to show that bio-based products may inhibit corrosion as well as their traditional oil-and solvent based counterparts, without any of the negative environmental considerations.

Economical study

In 2015 an estimated 300,000 tons of rust preventative fluids were used around the world—comprising approximately 12% of the total market for metalworking fluids. Asia uses about half of the world's supply of rust preventatives, driven in a large part by the enormous metal parts exporting industry in China. The remainder of the market is split about evenly between the Americas and Europe. European markets, where environmental regulations can be more stringent, use a higher percentage (about 40%) of water-based rust preventatives. Asian markets use solvent-based or oil-based protective fluids almost exclusively. These fluids also dominate in American markets, representing about 80% of market share [8].

Table 1 shows economic analysis, taking into consideration the total cost of bio-based and solvent-based products that are commercially available, collected from product data sheets.

The cost analysis is performed according to:
- Market price of the product
- Disposal cost, based on product classification waste number
- Transport cost, based on 100 liters of product
- Warehousing cost

Table 1. Rust preventative total cost per litre

Label	Manufacturer Product Name	Cost [EUR/l]	Disposal cost [EUR/l]	Transport cost [EUR/l]	Warehousing cost [EUR/l]	Total cost [EUR/l]	Protection time /indoor storage [months]
INH1	Cortec Corp. BioCorr	2.52	0.27	0.45	0.03	3.27	24
INH2	Fuchs Anticorit	4.44	0.573	0.45	0.03	5.49	12-36
INH3	Castrol Rustilo	4.75	0.427	0.56	0.04	5.78	9
INH4	Houghton Ensis	5.84	0.573	0.56	0.04	7.01	12
INH5	Fuchs Anticorit GB	2.99	0.427	0.56	0.04	4.02	6-12

Economic analysis showed that calculated total cost, including cost per litre, disposal, transportation, and warehousing is lowest for rust preventative INH1, and highest for rust preventative INH4. It should be noted that INH1 is bio-based, while INH4 is solvent based. Bio-based rust preventative INH1 shows lower total cost compared to four tested solvent based products (INH2, INH3, INH4, INH5), which makes it stand out as the most cost effective temporary corrosion protection product, while also being the most environmentally friendly.

Experimental study

In the experimental study, a series of analyses were conducted to evaluate both bio-based and petroleum-based rust preventatives. The first experimental analysis was accelerated corrosion testing using a humidity chamber, in an effort to simulate conditions experienced during transport and shipping. Second, each rust preventative was evaluated for cleanability. Easy removal ensures treated metal components can be quickly used, minimizing downtime and maximizing production output. The last analysis was electrochemical testing by means of polarization techniques, which determines efficiency of corrosion inhibition.

Materials and sample preparation

Five types of ready-to-use rust preventatives were evaluated: one bio-based which combines film-forming additives with vapour phase corrosion inhibitors (VpCI) and four conventional solvent- and oil- based products, which leave a temporary waxy protective film on metal surface. The properties of tested rust preventatives are given in table 2.

Table 2. Tested rust preventatives with properties taken from product data sheets

Identification	Manufacturer	Type	Density [g/cm³]	Flashpoint [°C]	General description
INH1	Cortec Corp. BioCorr	water/bio	1.00-1.01	not applicable	waterbased, biobased and biodegradable, VOC-free
INH2	Fuchs Anticorit	solvent	0.91	200	concentrate dilutable with white sprit (70:30)
INH3	Castrol Rustilo	solvent	0.8	> 38	dewatering properties, leaves an ultra-thin greasy film
INH4	Houghton Ensis	solvent	0.799	48	rust inhibitor that leaves waxy film
INH5	Fuchs Anticorit / GB	mineral base oils / solvent	0.79	40	mixture based on mineral base oils and corrosion preventative agents in volatile hydrocarbons

The carbon steel samples, dimension 60x100x1 mm, were polished with sandpaper (240 grit), immersed in methanol for five minutes, dipped in rust preventatives for 30 minutes, and then allowed to air dry for 24 hours before testing.

Humidity chamber testing

Humidity chamber testing was conducted according to ISO 6270-2 (modified ASTM D-1748), for a duration of 600 hours. The goal of this testing is to determine the resistance of different rust preventatives to an atmosphere of constant condensing humidity, RH 100% and 40 ± 3 °C, representing warehouse and/or transport environment. The testing was conducted in C&W Humidity cabinet, model AB5. Table 3 shows the film thickness measurement results using gravimetric method of applied rust preventatives after drying. The biggest film

thickness around 10 μm was measured for rust preventative INH2, whereas other rust preventatives left much lower film thickness, up to 2 μm.

Table 3. Thickness measurement of rust preventatives

Sample	Identification	Density [g/m³]	Weight of applied rust preventative [g]	Surface [m²]	Film thickness [μm]	Average film thickness [μm]
1	INH1	1000	0.0226	0.012	1.8833	1.3833
11			0.0106	0.012	0.8833	
2	INH2	910	0.1068	0.012	9.7802	10.2747
22			0.1176	0.012	10.7692	
3	INH3	800	0.0116	0.012	1.2083	1.2135
33			0.0117	0.012	1.2187	
4	INH4	799	0.0188	0.012	1.9608	2.0598
44			0.0207	0.012	2.1589	
5	INH5	790	0.0087	0.012	0.9177	0.8808
55			0.0080	0.012	0.8439	

Cleanability

After the rust preventative film has served its purpose, it has to be removed, commonly using alkaline degreasing cleaners. Clean removal of the rust preventative is essential to the performance of subsequent processing steps like painting, phosphating or galvanizing, or welding [8]. Evaluation of cleanability of rust preventatives was conducted by The Lubrizol Corp. in-house cleaning test. Panels coated with rust preventative are allowed to dry completely, and then immersed halfway in a 5% alkaline cleaning solution for 7.5 minutes at 45 °C. Afterward, the panels are rinsed with water and dipped into a copper sulphate plating solution. Successful removal of the rust preventative allows for more uniform copper plating on the panel surface. Harder to clean rust preventatives show gaps in the plating, indicating that the rust preventative was not well removed by the cleaner.

Electrochemical study

Electrochemical study of rust preventatives was conducted according to ASTM G-94. Treated samples were immersed in fresh water, for 1 hour and 5 days, respectively, at (23±2) °C. Measurements were carried out in standard three electrode test cell in relation to the reference saturated calomel electrode (SCE) with known interaction potential of +0,242 V versus standard hydrogen electrode (SHE). Polarization curves were registered after 30 minutes of exposure to aqueous solution, in order to allow corrosion potential (E_{corr}) stabilization. During the potentiostatic measurements, the working electrode was polarized to the potential of ± 250 mV relative to the corrosion potential and the current response was measured. The inhibitor efficiency was calculated from measured corrosion rate of unprotected and protected carbon steel samples.

Results and discussion

Resistance to constant-humidity condensation atmosphere

During and after 600 hours of humidity chamber testing, the treated panels were evaluated for pass/fail in accordance to ASTM D-1748. The standard states that a test surface shall pass if it contains no more than three dots of corrosion, no one of which is larger than 1 mm in

diameter, whereas, a test surface shall fail if it contains one or more dots of rust larger than 1 mm in diameter or if it contains four or more dots of any size. Corrosion occurring within 1/8" from the sides of the panel, or within 1/8" below the hanging holes is not counted. The humidity testing result are given in Figure 1.
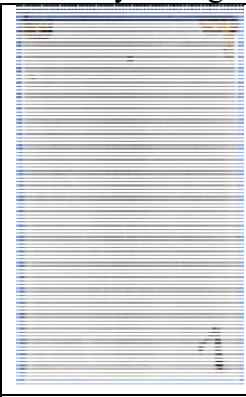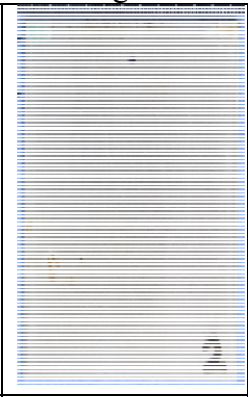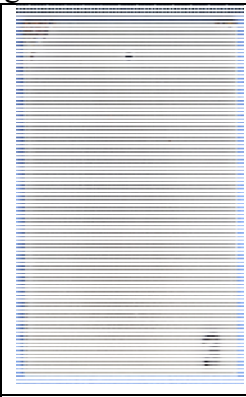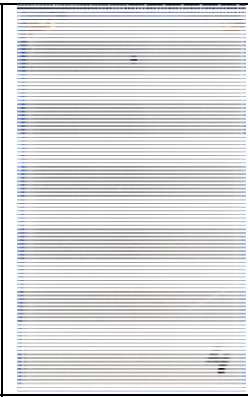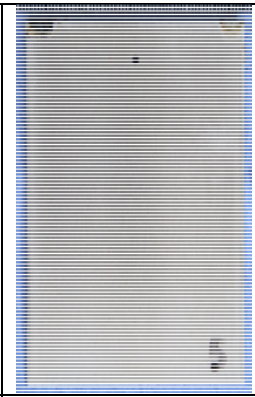

PASS, two corrosion spots observed smaller than 1 mm	FAIL, first signs of localized corrosion occur at 100 hours, larger than 1 mm	FAIL, four corrosion spots observed	PASS, one corrosion spot observed smaller than 1 mm	PASS, one corrosion spot observed smaller than 1 mm

Figure 1. Resistance evaluation of different rust preventatives to a constant-humidity (CH) condensation atmosphere

Compared to the petroleum derived products, the bio-based rust preventative showed excellent corrosion protection, after 600 hours in modified ASTM D-1748 testing. Rust preventative INH2, although thicker, didn't pass the testing, due to significant localized corrosion observed after 100 hours of testing in humidity chamber.

Cleanability evaluation

Cleanability testing was performed to determine the efficiency by which each rust preventative could be removed from a metal surface. A rust preventative film that is difficult to remove does not necessarily correlate with the best corrosion protection [8]. Increased removal time and effort leads to increased cost and lost time. Figure 2 shows an evaluation of cleanability test results. Rust preventatives INH1 and INH4 showed effective cleanability, while rust preventative INH2 showed moderate cleanability. Conversely, rust preventatives INH3 and INH5 showed insufficient cleanability, which meant the cleaning process had to be repeated. Evaluation was conducted based on pass/fail criteria.

PASS, effective cleanability	FAIL, 5% of surface still covered	FAIL, 30% of surface still covered	PASS, effective cleanability	FAIL, 70% of surface still covered

	with RP	with RP		with RP

Figure 2. Evaluation of the cleanability of rust preventatives (RP)

<u>Polarization measurements</u>

Figures 3 and 4 show the potentiodynamic polarization curves (Tafel diagrams) of unprotected carbon steel, alongside five rust preventatives, after 1 hour and after 120 hours in fresh water. Polarization measurements provide important information about the kinetics of anodic and cathodic reactions [9]. The corrosion parameters, namely corrosion potential (E_{corr}), corrosion current density (j_{corr}), corrosion rate (v_{corr}), anodic and cathodic Tafel slopes (β_a, β_c) are listed in Table 4 and 5.

According to the data presented, corrosion current density decreased with introduction of rust preventatives compared to unprotected carbon steel sample. The considerable corrosion potential shift to more noble values is observed with application of all rust preventatives, bio- and petroleum- based, indicating that tested rust preventatives greatly impacted the anodic reaction [10]. However, addition of rust preventatives also modified the cathodic polarization curves, indicating that tested rust preventatives exhibited both cathodic and anodic inhibition effects. Therefore, the studied rust preventatives function as a mixed-type inhibitor, showing reduced anodic dissolution and retarded the hydrogen evolution [11, 12]. In order to evaluate inhibition behaviour, an experiment without rust preventative addition was also performed. The blank curve exhibits more cathodic potential and higher current density.
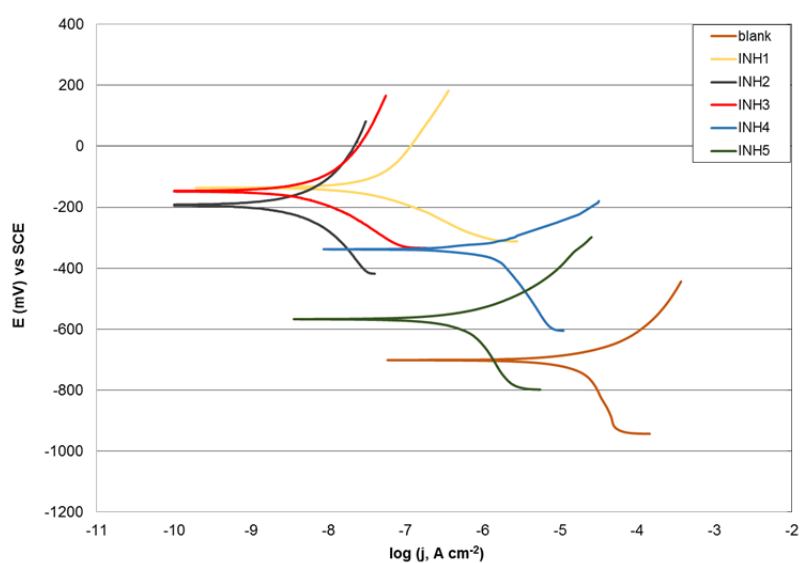

Figure 3. Polarization curves of tested rust preventatives, compared to unprotected carbon steel after 1 hour testing in fresh water
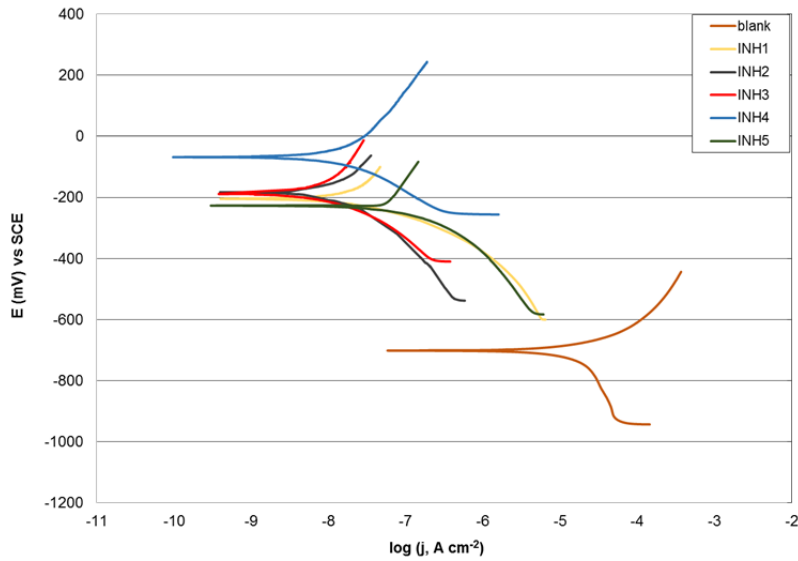
Figure 4. Polarization curves of tested rust preventatives compared to unprotected carbon steel after 120 hours testing in fresh water

Table 4. Polarization test results after 1 hour in fresh water, at a temperature (23±2) °C

Sample	E_{corr} [mV]	j_{corr} [μA/cm^2]	β_a [V/dek]	β_c [V/dek]	v_{corr} [mm/god]
blank	-686	25.87	117.1×10^{-3}	768×10^{-3}	170.8×10^{-3}
INH1	-136	55.18×10^{-3}	393.4×10^{-3}	136.9×10^{-3}	364.2×10^{-6}
INH2	-194	19.93×10^{-3}	942.1×10^{-3}	708.4×10^{-3}	131.6×10^{-6}
INH3	-149	10.16×10^{-3}	341.1×10^{-3}	203.5×10^{-3}	67.06×10^{-6}
INH4	-338	1.709×10^{-3}	123.4×10^{-3}	413.6×10^{-3}	11.28×10^{-3}
INH5	-567	841.9×10^{-3}	125.5×10^{-3}	553.6×10^{-3}	5.557×10^{-3}

Table 5. Polarization test results after 120 hours in fresh water, at a temperature (23±2) °C

Sample	E_{corr} [mV]	j_{corr} [μA/cm^2]	β_a [V/dek]	β_c [V/dek]	v_{corr} [mm/god]
blank	-686	25.87	117.1×10^{-3}	768	170.8×10^{-3}
INH1	-205	27.99×10^{-3}	445.8×10^{-3}	82.37×10^{-3}	184.7×10^{-6}
INH2	-182	13.22×10^{-3}	128.3×10^{-3}	214.4×10^{-3}	87.25×10^{-6}
INH3	-193	9.957×10^{-3}	398.5×10^{-3}	82.40×10^{-3}	65.72×10^{-6}
INH4	-67	26.23×10^{-3}	374.2×10^{-3}	176.5×10^{-3}	173.1×10^{-6}
INH5	-226	76.10×10^{-3}	174.3×10^{-3}	110.3×10^{-3}	502.3×10^{-6}

After 120 hours of exposure in fresh water, all tested rust preventatives showed similar corrosion protection taking equal potential-current position and shape in Tafel diagram, Figure 4. Only rust preventative INH4 showed a slightly higher potential shift. Compared to corrosion behaviour at the beginning of exposure, after 120 hours all tested rust preventatives showed improved inhibition efficiency, which can be attributed to a longer period for film forming on the metal surface.

The corrosion inhibition efficiency (η) after 1 and 120 hours of testing was calculated using the relation (1):

$$\eta_i = \frac{(v_{corr})_{ni} - (v_{corr})_i}{(v_{corr})_{ni}} \cdot 100\% \quad (1)\,[3]$$

where $(v_{corr})_{ni}$ and $(v_{corr})_i$ are uninhibited and inhibited corrosion rates, respectively, obtained from potentiodynamic polarization curves. The increased η values show that the inhibition is more pronounced. Based on measured corrosion rate of unprotected compared to protected carbon steel, inhibition efficiency of tested rust preventatives was calculated and results are given in Figure 5. Maximum inhibition efficiency obtained from potentiodynamic polarization was with rust preventatives INH3, INH2, and INH1 respectively, whereas rust preventatives INH 5 and INH 4 showed something lower inhibition after 1 hour of exposure to fresh water. After 120 hours, all tested rust preventatives showed over 99 % inhibition efficiency. INH1, which is a water/bio-based rust preventative, showed constant inhibition efficiency at the beginning and end of test, which demonstrates fast film adsorption properties. The solvent based rust preventative INH5 showed the lowest improvement in corrosion resistance among all tested rust preventatives. However, corrosion resistance was improved by approximately 1000 times better, compared to the unprotected sample.
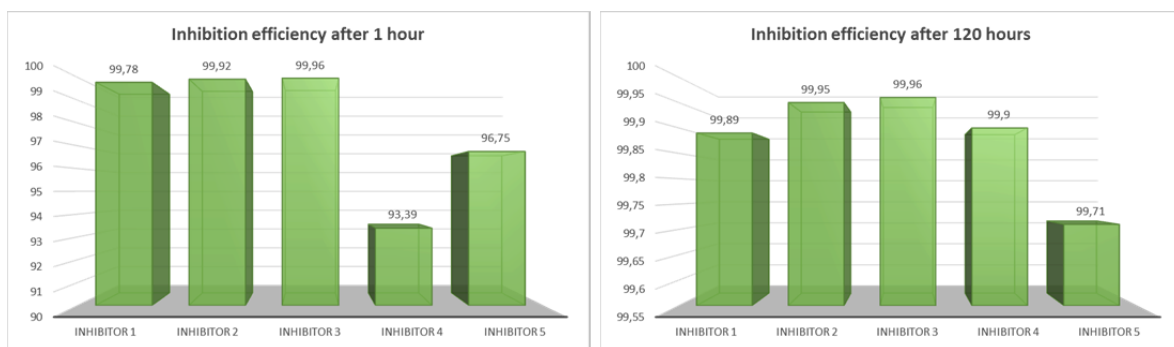

Figure 5. Inhibition efficiency of rust preventatives after 1 hour (left) and 120 hours (right) in testing solution.

Conclusions

Choosing the proper rust preventative is not only based durability and effectiveness, but also removal and disposal concerns. A proper selection of rust preventative depends on storage and/or transport conditions, protection period, and also their economic and environmental impact.
In this paper, the corrosion parameters as well as economic and environmental properties of five different rust preventatives used for temporary corrosion protection. Specifically, water/biobased was compared to petroleum based products.

The results of this study are summarized as follows:
- Three of the five rust preventatives passed 600 hours of high humidity testing. This included the biobased product, along with two of the solvent based products. The remaining two solvent based products failed during the test period.

- Higher thickness of rust preventative didn't provide better corrosion protection. Further, this increased thickness had a negative influence on cleanability.
- In addition to being more environmentally friendly, biobased rust preventatives offer optimal corrosion protection, with no increase in protection cost, compared to petroleum-based and hazardous rust preventatives.

Following the results from this study, biobased preventative is an excellent and environmentally acceptable alternative to petroleum based products in temporary corrosion protection.

References

[1] Boris A. Mikšić, FNACE: VpCI Technology Handbook, vol. 1, USA, 2014.

[2] M. Kharshan, C. Cracauer: The New Generation of Rust Preventative Products Based on Renewable Materials and Incorporating Vapor Corrosion Inhibitors, NACE Conference & Expo "Corrosion 2010", Paper No. 10147.

[3] F. Ivušic, O. Lahodny-Šarc, H. Otmačić Ćurković, V. Alar, Corrosion Science, **98** (2015) 88–97.

[4] J. H. W. de Wit, D. H. van der Weijde, G. Ferrari: „Organic coatings" in Corrosion Mechanisms in Theory and Practice, Second Edition, Ed. P. Marcus, Marcel Dekker, Inc., USA (2002) pp. 683 – 729.

[5] Giles J. P. Becket: „Corrosion: Causes and Cures" in Metalworking Fluids, Second Edition, Ed. J. P. Byers, Taylor & Francis Group, USA (2006) pp. 175 – 194.

[6] A. Ghanbarzadeh, E. Akbarinezhad, Progress in Organic Coatings, **56** (2006) 39–45.

[7] M. Vitthal Khaire, M. Nilavan, A. Jain, IOSR Journal of Mechanical and Civil Engineering, **13** (2016) 82-90.

[8] G. Moran, B. Faber, Tribology & lubrication technology, **72** (2016) 28-34.

[9] A. Ehsani, H. Mohammad Shiri, M. G. Mahjani, R. Moshrefi, R. Safari, Kovove Mater, **54** (2016) 233–239.

[10] Camila G. Dariva and Alexandre F. Galio: "Corrosion Inhibitors – Principles, Mechanisms and Applications" in Developments in Corrosion Protection, Ed. M. Aliofkhazraei, InTech, (2014) pp. 365-379.

[11] Olivares, O., Likhanova, N.V., Gomez, B., Navarrete, J., LlanosSerrano, M.E., Arce, E., Hallen, J.M., Appl. Surf. Sci., **252** (2006) 2894– 2909.

[12] R. Karthikaiselvi, S. Subhashini, Journal of the Association of Arab Universities for Basic and Applied Sciences, **16** (2014) 74–82.